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ION COMPOSITION AND ION CHEMISTRY IN AN AURORA

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IN AN AURORA

(Planetary and Space Science)

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ABSTRACT

Ion composition measurements are reported as obtained with a rocket borne mass spectrometer flown during an aurora. At the level of highest ion production near 115 km the NO^+ density was a factor of 3 larger and the O_2^+ density a factor of 10 smaller than expected from normal composition, temperature and ion chemistry models. The O^+ density was a factor of 50 larger than expected. The results appear to demand effective ion temperatures greater than 1000°K and electron temperatures even larger. They also require efficient channels for conversion of O_2^+ to NO^+ . Reactions of O_2^+ with anomalously abundant NO or N with vibrationally excited N_2 are regarded as possible modes for transforming O_2^+ into NO^+ . Densities of He^+ in excess of 50 cm^{-3} were observed and not understood.

The O_2^+ densities measured are too low to permit dissociative recombination to contribute significantly to OI green line excitation except at high altitude.

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1. INTRODUCTION

In a recent analysis of the results of a number of sounding rocket experiments Donahue et al. (1968) arrived at the conclusion that dissociative recombination of O_2^+ was the preponderant source of excitation for the 1S term of atomic oxygen in the aurora. They reported measurements of the local volume emission rates of the $OI\ 5577\text{\AA}$ line, the N_2^+ first negative (0 - 0) band at 3914\AA among many other emission features and some measurements of the electron flux. From these they showed that direct excitation of the $O(^1S)$ term from ground state oxygen required cross sections orders of magnitude too large to be acceptable. They also showed that dissociative excitation of $O(^1S)$ from O_2 required an effective cross section which was rather large and which had to increase with altitude relative to the cross section for excitation of the 3914\AA band. On the other hand the observed excitation rate of $O(^1S)$ agreed closely with one fifth of the total computed rate of creation of O_2^+ . This rate was deduced by reducing the observed rate of production of the 3914\AA band to the rate of ionization of N_2 and by using a model atmosphere and conventional ion chemistry to infer the rates of O^+ , O_2^+ and NO^+ production from those for N_2^+ . The branching ratio of O_2^+ recombination into the $O(^1S)$ state was one measured in the laboratory by Zipf (1967).

To test the validity of this proposed mechanism a sounding rocket experiment was flown from Ft. Churchill during the night of February 8, 1968 (NASA Aerobee 4.217 UA). In addition to visual and ultraviolet upward looking and downward looking photometers and electron energy analyzing spectrometers the experiment package contained a quadrupole ion mass spectrometer. This mass filter measured the density of ionic species

between 96 km and 157 km. Its principal purpose was to provide measurements of O_2^+ densities for comparison with the 5577A volume emission rates observed by one of the photometers. The result of that experiment, to be reported here was the discovery that the O_2^+ density was far too low to provide an adequate supply of $O(^1S)$ atoms to excite the green line to the level observed. At low altitude where excitation was strongest O_2^+ recombination could account for only a few percent of the 1S atoms needed. The relative contribution from O_2^+ was found to increase with altitude, however, until at 130 km it was responsible for about half of the excitation. This finding has led us to reassess the role of dissociative excitation from O_2 in creating 1S atoms (Donahue et al., 1969). We now regard this as the principal source of excitation for the green line at low altitudes in the aurora, although dissociative recombination plays an increasingly important role as the altitude increases. This mechanism removes the difficulty with the pathological altitude dependence of the cross section for electrons dissociating O_2 into 1S atoms mentioned above.

The ion densities measured present interesting new problems for the ion chemistry or atmospheric composition in auroras. NO^+ was found to be the predominant ion. The ratio of NO^+ to O_2^+ was so large that a mechanism must be found to convert O_2^+ efficiently to NO^+ during an aurora, a mechanism which does not exist in the normal mid-latitude daytime ionosphere. Among the possibilities are large densities of NO and or N with which O_2^+ can react or high N_2 vibrational "temperatures" which might increase the rate constant for the reaction



two orders of magnitude above its value at 300°K. It was also found that the O^+ densities were very high. This appears to indicate that the effective kinetic temperature of O^+ was well above 1000°K between 110 km and 120 km, causing the rate constants for O^+ conversion to O_2^+ and NO^+ to be small, or that the atomic oxygen density was greatly enhanced. Dissociative recombination coefficients inferred from the ion densities - particularly for NO^+ - suggest electron temperatures increasing from about 350°K at 107 km to 1700°K at 132 km. Very large He^+ densities were also observed - in excess of 50 ions per cc. The disparity between He^+ observations on up-leg and down-leg, the extraordinarily high concentrations found, and the realization that the Aerobee tanks are pressurized with helium causes us to regard these observations with some skepticism. Confirmation with spectrometers carried on solid fueled rockets is called for.

2. INSTRUMENTATION

The components of the rocket payload most relevant to the purposes of this paper were two: a three channel photometer and the ion mass spectrometer. The characteristics of the photometer will be discussed in full detail in a subsequent paper devoted to optical effects in auroras. Briefly it consisted of three independent interference filter-photomultiplier units sighted parallel to the spin axis of the rocket. The filters were selected to transmit the OI ($2^1S - 2^1D$) auroral green line at 5577\AA , the N_2^+ ($B^2\Sigma_u^+ - X^2\Sigma_g^+$) first negative ($0 - 0$) band at 3914\AA and the N_2 ($B^3\Pi_g - A^1\Sigma_u$) first positive ($5 - 2$) band at 6685\AA . Important supplementary

information concerning optical excitation was obtained from a two channel up-down photometer sensitive to the OI ($2^1S - 2^3P$) trans-auroral line at $2972\overset{\circ}{\text{\AA}}$ and bands in the second positive system of N_2 at nearby wavelengths. (K. Dick and W. G. Fastie, private communication.)

The quadrupole ion mass filter was designed to measure the densities of positive ions from mass number 3 through 40. The instrument weighed only 14 lbs., used solid state circuitry throughout, and under flight conditions had a nominal mass resolution of about 60. The basic quadrupole lens was formed by four stainless steel rods that had been carefully stress relieved and centerless ground to assure a high degree of dimensional accuracy and stability. The rods were 7.000 mm in diameter and 100 mm long, and they were equidistantly spaced with their centers 6.517 mm from the axis of the spectrometer. The diameter of the injection aperture was 0.50 mm and the axis of symmetry of the mass filter was located on the spin axis of the rocket.

The quadrupole lens was held in a cylindrical stainless steel housing with a large pumping conductance so that the mass spectrometer vented very rapidly. The support housing was insulated from the rocket body and was maintained at a potential of - 9.1 volts with respect to the vehicle. A high transparency, stainless steel screen was placed 15 mm in front of the injection aperture. The screen was operated at a potential of - 2.6 volts with respect to the aperture in order to provide a suitable draw-in field. Careful alignment of the central hole in the square mesh with the axis of the instrument provided an almost uniform field between the grid and the injection aperture.

Ion detection was provided by a Bendix Channeltron mounted behind the exit aperture. This detector was located so that it was protected from

ultraviolet radiation passing through the mass spectrometer apertures. The cathode was maintained at - 1340 volts to draw ions transmitted by the mass filter into the channeltron. A 200 volt collector bias was supplied between the anode of the channeltron and a stainless steel Faraday cup. The collected ion current was measured by an electrometer that had two analog ranges separately telemetered: (1) a linear output for input currents between 2×10^{-11} to 2×10^{-9} amperes and (2) a non-linear scale for currents ranging from 1×10^{-9} amperes to 5×10^{-7} amperes. The electrometer had 10 msec time response.

The mass filter was operated at a fixed radio frequency of 3.5 MHz and was voltage scanned in a constant mass resolution mode. Although the mass spectrometer nominally scanned from mass number 3 through 40, the voltage waveform that programmed the mass sweep maximized the observation time in the range 10 - 40 amu at the expense of the still lighter ions. This was done to optimize the measurement of the O_2^+ density and the densities of the other major atmospheric ions that were expected on the basis of our earlier results.

The final calibration of the mass spectrometer was performed in the field at Ft. Churchill. Our portable vacuum system was equipped with a low energy electron gun that created a cloud of positive ions with thermal energies in front of the ion mass spectrometer. By introducing additional apertures between the ion cloud and the top of the mass spectrometer, we found that the spatial distribution of the ions was uniform over the collection area and that the detected currents scaled with the proper geometric factor when the diameter of the collimating aperture was changed. By monitoring the current to the grid, to the plate containing the input aperture, and the current transmitted by the quadrupole lens,

we were able to determine the sensitivity of the mass spectrometer as a function of the incident ion flux density. From these measurements we estimated the ambient ion density by assuming that the detected ions had kinetic energies equal to the full 2.6 electron volts provided by the draw-in field and that the uniformity of the field in the region between the ionizer and grid assured that the beam was well collimated.

During the flight the ions entering the mass spectrometer had an additional component of velocity along the axis of the instrument caused by the rocket motion that must be taken into account when using the laboratory calibration. In deriving the corrected value we relied on the trajectory data provided by ground-based radar and a DOVAP transponder on board the rocket and aspect data provided by the flight magnetometers. The vehicle potential was not measured in this experiment and a systematic error in the measured densities will result if the rocket's potential in the actual experiment was large. We further assumed in estimating the absolute ion densities, that the positive ions were in thermal equilibrium with no appreciable mass motion (high drift velocities, for example, due to local electric fields).

During the flight the resolution of the mass spectrometer was observed to change slowly with time. Since the transmission of the spectrometer depends on the resolution, the transmission had to be corrected as a function of flight time for each mass species. The final, overall absolute calibration is probably good to within a factor of 2 with the exception of He^+ where the results are less reliable (factor of 4); the relative calibration is, of course, much better.

A sample spectrum reproduced from the paper telemetry record obtained during flight is shown in Fig. 1.

3. RESULTS

The signal observed by the 3914Å^o photometer during rocket ascent began to decrease when the rocket was at 88 km. The up-down photometer results, as well as the ground based photometer record, show that the excitation was stable in time while the rocket rose from 88 km to 123 km. When the rocket was at the 123 km level the photometers began to sense a brightening of the aurora overhead. The up-down photometers, the ion-mass spectrometer and the electron spectrometers showed that the rocket entered a region affected by enhanced excitation at 127 km and emerged from it at 136 km. The electron flux above 136 km remained somewhat higher than it had been below 127 km, however. With the help of data from these instruments the purely temporal effects have been subtracted from the 3914Å^o signal above 123 km and an extrapolation of the pre-disturbance height profile obtained. The gradient of the overhead emission rate in photons/cm²sec gives the volume emission rate for the N₂⁺ 3914Å^o emission and is plotted in Fig. 2.

The ion-densities, corrected for vehicle motion and instrumental transmission variations are plotted in Fig. 2 as a function of altitude. The effects of the pulse of ionization into which the rocket penetrated at 127 km are clearly visible beginning at that altitude. The O⁺, O₂⁺ and N₂⁺ densities apparently returned to their "normal" values shortly after the pulse had passed while the NO⁺ density seems to have decayed slowly. Our guess at the densities which would have existed had the enhancement not occurred are indicated by broken lines in the figure.

In these data several interesting features appear.

- 1) The O_2^+ densities are far lower than anticipated (Donahue et al., 1968) and are clearly not large enough to provide an adequate supply of $O(^1S)$ atoms through dissociative recombination for excitation of the green line to the level observed. This is to say that the density of O_2^+ is at least an order of magnitude smaller than conventional models of atmospheric composition and chemistry would predict.
- 2) The NO^+ densities observed are higher than expected on an absolute basis and in relation to O_2^+ densities.
- 3) The O^+ densities, especially at low altitudes, are larger than expected.
- 4) The ion densities do not begin to be measureable until the rocket is at 100 km, despite the occurrence of considerable N_2^+ excitation (and therefore ionization) below this altitude.

4. ANALYSIS

To cast these comments in quantitative form it is necessary to calculate ionization rates and reaction rates based on model atmospheres. No measurements of neutral densities were performed during this experiment. The model we have chosen above 120 km is one developed by Zipf (1966) to account for dayglow observations. It does not differ significantly from models suggested by Walker (1965) and Bates (1959) in the regime of altitudes of interest in this analysis. Below 120 km the densities conform to the semi-theoretical Anderson and Francis (1966) model. The exospheric temperature according to Jaccia's (1965) empirical model was 1087° . The model densities are given in Table 1.

Table 1: Model Atmosphere Used For Calculations

<u>z</u> <u>km</u>	<u>n(O)</u> <u>cm⁻³</u>	<u>n(O₂)</u> <u>cm⁻³</u>	<u>n(N₂)</u> <u>cm⁻³</u>	<u>T</u> <u>°K</u>
100	5.8 ^{11*}	1.90 ¹²	7.8 ¹²	
102	4.6	1.25	5.2	
105	3.3	7.3 ¹¹	3.0	
107	2.7	5.0	2.1	
110	2.0	2.9	1.30	
113	1.45	1.80	8.1 ¹¹	
116	1.10	1.10	5.2	
120	8.0 ¹⁰	6.0 ¹⁰	3.0	310
125	5.6	3.1	1.70	337
130	3.9	1.70	9.8 ¹⁰	368
135	2.8	9.9 ⁹	6.0	402
140	2.1	5.8	3.7	440
145	1.60	3.6	2.4	480
150	1.20	2.3	1.65	521
155	9.6 ⁹	1.55	1.15	560
160	7.7	1.05	8.1 ⁹	598
165	6.3	7.5 ⁸	5.9	633
170	5.2	5.4	4.4	665

*5.8¹¹ means 5.8 x 10¹¹

The rate of ionization of N_2 , taken to be 17 times the volume emission rate of the 3914Å band. Making use of the observation that the cross section for the process



averages about 0.8 times that for ionization of nitrogen, (Rapp and Golden, 1965) the rate of production of O_2^+ ions by electrons Q_3 was calculated from

$$Q_3 = 0.8Q_2 n(O_2)/n(N_2) \quad (3)$$

On the average one third of all ions produced by electrons incident on O_2 are O^+ ions resulting from dissociative ionization. (Fite and Brackmann, 1959.) In addition to this source of O^+ , direct ionization of O will contribute to Q_1 , the rate of O^+ production, with an average cross section about 0.65 that for ionization of N_2 (Fite and Brackmann, 1959). Hence the total rate of O^+ formation is given by

$$Q_1 = 0.5Q_3 + 0.65Q_2 n(O)/n(N_2) \quad (4)$$

Since there is no important source of O^+ other than direct ionization of O and O_2 the steady state equation for O^+ is

$$Q_1 = k_b n_1^+ n_3 + k_c n_1^+ n_2 = n_1^+ / \tau_1 \quad (5)$$

Here the subscripts have the following significance

1 : 0

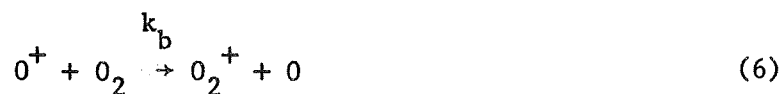
2 : N₂

3 : O₂

4 : NO

5 : N

k_b is the rate constant for the process



while k_c is the rate constant for the reaction



From the relationship (5), and the measured value of n_1^+ it is possible to compute the value required for τ_1 or for

$$k_b + (n_2/n_3)k_c = (\tau_1 n_3)^{-1} \quad (8)$$

The temperature dependence of k_b and k_c has been measured by Dunkin et al. (1968) between 80° and 600°K and the dependence of k_c on the vibrational temperature of N₂ when the gas and ion temperatures are 300°K by Schmeltekopf et al. (1968). Guided by these measurements but unfortunately forced to extrapolate sometimes to temperatures above 600°K, we can put limits on k_b and k_c from the value we have obtained for $(\tau_1 n_3)^{-1}$. The largest value possible for k_b is one satisfying equation (8) when the

corresponding value for k_c is appropriate to the same temperature. Values of k_b smaller than this and implying larger kinetic temperatures require that k_c be larger than the minimum value thus obtained. These combinations of k_b and k_c might, however, be appropriate if high kinetic temperatures and high vibrational excitation of N_2 coexist.

The branching ratios

$$r_{13} = k_b n_3 n_1^+ / Q_1 \quad (9)$$

going to O_2^+ and

$$r_{14} = k_c n_2 n_1^+ / Q_1 \quad (10)$$

going to NO^+ are thus undetermined. Since there is a problem arising from the measurement of low O_2^+ densities and high NO^+ densities we have selected values of k_b and k_c which correspond to kinetic temperatures well above the smallest possible values. This will enhance r_{14} in comparison with r_{13} .

We have assumed that the fractions of Q_2 leading to ionization of O_2^+ by the charge transfer reactions



leading to production of NO^+ by the reaction



were given by

$$r_{23} = \frac{k_a n(O_2)}{k_a n(O_2) + k_d n(O)} \quad (13)$$

and

$$r_{24} = \frac{k_d n(O)}{k_a n(O_2) + k_d n(O)} \quad (14)$$

Here k_a was chosen to be the value at the same temperature appropriate for k_b , and k_d was assumed to be independent of temperature at $2.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

With the branching ratios r_{13} and r_{23} determined the total rate of production of O_2^+ is given by

$$Q_3' = Q_3 + r_{13}Q_1 + r_{23}Q_2 \quad (15)$$

Loss of O_2^+ can occur by dissociative recombination at a rate $\alpha_3 n_3^+ n_e$ where

$$n_e = n_1^+ + n_3^+ + n_4^+ \quad (16)$$

and by the reactions





at a rate n_3^+/τ_3' . Thus the continuity equation for O_2^+ takes the form

$$Q_3' = \alpha_3 n_3^+ n_e + n_3^+/\tau_3' \quad (20)$$

All three of the processes, (17), (18) and (19), convert O_2^+ to NO^+ . All except process (19) were assumed to proceed at their room temperature rates. However, the selection of the relative amounts of Q_3' which go into the two channels of recombination and conversion to NO^+ depends on the choice of α_3 , and thus on the electron temperature. The values selected for α_3 and α_4 for NO^+ must be mutually consistent. The value of τ_3' in (20) was therefore adjusted until α_3 and α_4 acquired values appropriate to the same T_e .

The NO^+ recombination coefficient α_4 was obtained from the NO^+ continuity equation

$$r_{14}Q_1 + r_{24}Q_2 + n_3^+/\tau_3' = \alpha_4 n_4^+ n_e \quad (21)$$

The nature of the problems presented by these measurements is revealed if this analysis is carried out for the data obtained at 116 km, the lowest altitude at which good ion density measurements were available for O_2^+ and O^+ . The 3914Å emission rate was $2.2 \times 10^2 \text{ cm}^{-3} \text{ sec}^{-1}$ at 116 km. The densities and ionization rates at that altitude are given in Table 2. From equation (5) then τ_1^{-1} is found to be 0.45 sec^{-1} and

$$k_b + 4.7 k_c = 4.2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (22)$$

Table 2
(Conditions at 116 km)

Neutral Densities
(cm⁻³)

$$n_2 = 5.2 \times 10^{11}$$

$$n_3 = 1.1 \times 10^{11}$$

$$n_1 = 1.1 \times 10^{11}$$

Production
(cm⁻³ sec⁻¹)

$$Q_2 = 3.7 \times 10^3$$

$$Q_3 = 6.3 \times 10^2$$

$$Q_1 = 3.1 \times 10^2 + 5.1 \times 10^2$$

Ion Densities
(cm⁻³)

$$n_4^+ = 2.3 \times 10^5$$

$$n_3^+ = 0.11 \times 10^5$$

$$n_1^+ = 1.8 \times 10^3$$

Although the model temperature at 116 km is below 300°K, there is no reason to suppose that during an aurora the effective temperature of O^+ is so low. Indeed the condition on k_b and k_c is obviously irreconcilable with the values

$$k_b = 2.1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (23)$$

and

$$k_c = 1.0 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (24)$$

measured at 300°K. If we suppose that the trend observed by Dunkin et al. (1968) for the variations of k_b and k_c with temperature continues to temperatures higher than 600°K then the only consistent pair of values are

$$k_b = 3.7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (25)$$

$$k_c = 1.1 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (26)$$

which occur at 1120°K when N_2 is not excited. Smaller values of k_b and larger values of T_1 are possible if k_c depends on the vibrational state of N_2 and N_2 is excited. Thus T_1 might be as high as 1400°K and the rate constants given by

$$k_b = 2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (27)$$

$$k_c = 4 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (28)$$

The rate constant k_c would only be $5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ if the nitrogen vibrational temperature were also 1400°K .

If we assume that T_i is 1200°K , with

$$k_b = 3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (29)$$

and

$$k_c = 2.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (30)$$

then

$$r_{13}Q_1 = 6 \times 10^2 \text{ cm}^{-3} \text{ sec}^{-1} \quad (31)$$

$$r_{14}Q_1 = 2.2 \times 10^2 \text{ cm}^{-3} \text{ sec}^{-1} \quad (32)$$

As for N_2^+ , since n_1 and n_3 are equal, r_{24} is 2.5 times as large as r_{23} and

$$r_{23}Q_2 = 1.1 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1} \quad (33)$$

$$r_{24}Q_2 = 2.6 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1} \quad (34)$$

Hence Q_3' will be $2.3 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ and α_3 would need to be $9 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ if all of this production was to be removed by recombination alone. Thus a large part of the O_2^+ density must be transformed to NO^+ . In fact the steady state conditions for O_2^+ and NO^+ are

$$2.3 \times 10^3 - \frac{1.1 \times 10^4}{\tau_3} = 2.65 \times 10^9 \alpha_3 \quad (35)$$

and

$$2.8 \times 10^3 + \frac{1.1 \times 10^4}{\tau_3} = 5.5 \times 10^{10} \alpha_4 \quad (36)$$

When these conditions have been combined they require that

$$\alpha_4 + 4.8 \times 10^{-2} \alpha_3 = 9.3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \quad (37)$$

This equation can be satisfied by compatible coefficients only at an electron temperature of 1400°K (Mehr and Biondi, 1969 and Weller and Biondi, 1968), where

$$\alpha_4 = 9 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \quad (38)$$

and

$$\alpha_3 = 6.3 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \quad (39)$$

With these values for the recombination coefficients the O_2^+ loss to NO^+ must occur at a rate satisfying

$$\frac{1.1 \times 10^4}{\tau_3} = 2.14 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1} \quad (40)$$

$$\frac{1}{\tau_3} = 0.2 \text{ sec}^{-1} \quad (41)$$

or

$$n_5 + 4.4 n_4 + 3 \times 10^{21} k_g = 1.1 \times 10^9 \text{ cm}^{-3} \quad (42)$$

For the densities and the rate constants separately this condition sets the following upper limits:

$$n_5 \leq 1.1 \times 10^9 \text{ cm}^{-3} \quad (43)$$

$$n_4 \leq 2.5 \times 10^8 \text{ cm}^{-3} \quad (44)$$

$$k_g \leq 3.7 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (45)$$

Unless k_g is considerably greater than the upper limit of $10^{-15} \text{ cm}^3 \text{ sec}^{-1}$ measured for N_2 at 300°K the conditions placed on the nitrogen and nitric oxide densities are severe. There is a possibility, however, that the rate constant is higher when the nitrogen is excited.

This analysis has been carried out for the entire range of altitudes covered during the upleg of the auroral flight. Results are plotted in Figs. 3 and 4. These show the values of $k_b + k_c (n_2/n_3)$

required to account for the O^+ densities, the range of values for k_b and k_c consistent with them and not requiring more than an order of magnitude enhancement of k_c because of vibrational excitation of N_2 . Also plotted are the range of O^+ temperatures corresponding to these values of the rate constants. Upper limits for n_5 , n_4 and k_g as set by the O_2^+ and NO^+ densities are also plotted. From the values which the recombination coefficients must assume the electron temperature is shown also as a function of altitude.

Below 116 km the O^+ and O_2^+ densities become too small to be read adequately from the data records. Thus only lower limits can be set on the removal rates and associated rate constants or densities. However, the NO^+ density decreases below 115 km while the maximum in the ionization rate implied by the 3914A^o signal occurs much lower. Thus it appears that α_4 must increase below 115 km. At 107 km the value computed for α_4 is $4.1 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. This corresponds to an electron temperature of only 350°K. It would seem that the electron temperature must rise rapidly between 107 km and 110 km to about 1200°K and then increases somewhat more slowly to 2500°K at 140 km. The values shown above 140 km are somewhat uncertain because of the effect of the excitation wave encountered.

If the thermal profile implied by the O^+ loss rate were identified with the gas temperature some serious physical problems would arise. It seems much more reasonable to regard this temperature as being some sort of effective temperature for the O^+ ions. The fraction of all the O^+ ions produced which originate from dissociative ionization of O_2 decreases from 0.53 to 0.14 between 107 km and 140 km. A large part of the ions thus created will initially have kinetic energies in excess of 1 eV. However,

the thermalization time for 1 eV O^+ ions at 120 km is only about .02 seconds, while the chemical time constant is about 3 seconds. Thus the bottle neck in oxygen ion removal cannot be in slowing down this initially energetic O^+ component. This being the case we must consider our results as indicating that there existed a source of ionic heating capable of creating ion temperatures in excess of $1000^\circ K$ between 110 km and 120 km during this aurora. The constraint $T_i \leq T_e$ would require that the ion temperature begin to decrease rapidly below 110 km, if the calculated value of α_4 below 110 km correctly represents the recombination coefficient at these altitudes.

However, there is every reason to believe that if the mass spectrometer was functioning properly no steady state relating purely local ion production and loss prevailed at low altitudes. The reason is that the ion mass spectrometer was able to measure no ions at all in the region from 96 km to 100 km. And yet there was obviously ionization at a rather high rate in this region as evinced by the 3914A^o signal. The up-down photometer (K. Dick, private communication) clearly showed that the rocket entered the aurora at 88 km and that by the time it reached 100 km there was a lot of emission below it. In brief this instrument justified the emission profile which we have shown in Fig. 2. We are forced therefore to conclude that for some reason the ion densities inferred from the mass spectrometer currents cannot be related to local ion production rates by local steady state production and loss up to at least 105 km. In fact, it is very doubtful that they can be so related below 110 km. (At 100 km the recombination coefficient would have to be $10^{-5} \text{ cm}^3 \text{ sec}^{-1}$ to reconcile the local production rate and the NO^+ density). We shall return to this point

subsequently, but here shall suggest that sufficiently high large vertical electric field components exist in the aurora that the positive ions created below 105 km drift upward with such high velocities that the mass spectrometer samples then inefficiently. We also suggest that these fields may be responsible for the heating or large drift velocities which produce the elevated ion "temperatures" about 110 km. Optical evidence for such electric fields will be discussed in subsequent sections.

We can offer an alternative ad hoc explanation for the large O^+ densities observed by postulating larger atomic oxygen densities than those in our model. Consistency requires that we reduce the O_2 density accordingly. The values of $k_b + (n_2/n_3)k_c$ needed when n_1 is doubled (and n_3 reduced by a factor of 5) were computed. If n_1 is doubled k_b could be as high as $7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at 116 km, k_c $2.4 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ and $T(O^+)$ 800°K. If n_1 is quadrupled and n_3 halved $T(O^+)$ could be 400°K with

$$k_b = 1.7 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (46)$$

$$k_c = 0.8 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (47)$$

Such a solution for the O^+ problem at low altitudes leads to unacceptably large rate constants at high altitude if the oxygen is assumed to be in diffusive equilibrium. Oxygen densities ranging from 4 times our model values at 116 km to 1.5 times these values at 132 km would be needed to produce the observed ion densities and production rates with rate constants proper to temperatures between 250°K and 400°K.

Of the three possible channels for conversion of O_2^+ to NO^+ with the high efficiency called for by these measurements selection of those effective during the aurora can be made only on grounds of plausibility. The contrast between these conditions and those in the normal mid-latitude daytime ionosphere where O_2^+ and NO^+ densities are about equal calls for some severe modification in the composition of the atmosphere at high latitudes or during an auroral display. (We count a change in vibrational excitation as a change in composition.) Thus if atomic nitrogen densities were as high as 10^9 cm^{-3} at 116 km during the aurora they could not ordinarily be so large at lower latitudes. The NO densities required are about 500 times larger than those measured by Barth (1966). There is an enhancement of nitrogen atom production during an aurora, because almost every N_2^+ ion and about one in every two O^+ ions produce two fresh nitrogen atoms. Hence N atoms were being created at 116 km at a rate of about $8 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$. Although the aurora had been almost 10 times as bright a few minutes before the rocket reached it, it had, after all, been affecting the region studied for only a very small part of a day. Hence it seems unreasonable to expect auroral electrons to have produced the modification in composition needed to account for the conversion of O_2^+ to NO^+ . Furthermore the altitude profile required of N is peculiar in that the scale height called for is only about half that of atomic oxygen. If the species responsible is NO the scale height requirements are reasonable.

Until laboratory measurements are carried out it is not possible to say whether rate constants of between 2 and $3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ are reasonable for a reaction between O_2^+ and N_2 excited to a high vibrational "temperature" in the aurora. It is interesting that the effective rate constant needed is almost independent of altitude. This suggests that if

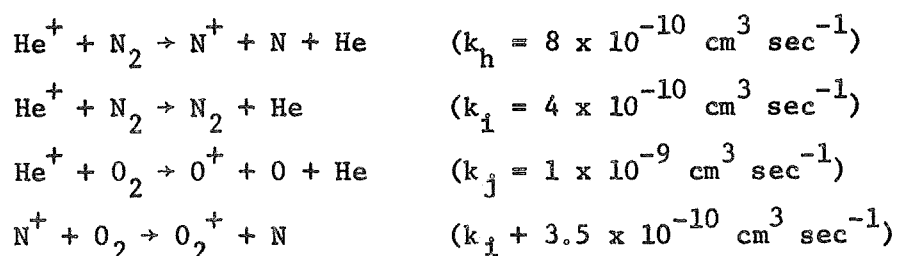
this mechanism is to explain the phenomenon the degree of N_2 excitation must be relatively constant between 107 km and 130 km or some compensation occurs between effects of changing O_2^+ temperature and N_2 vibrational distribution. Presumably vibrational excitation would occur in collisions with slow secondary electrons, while quenching would involve collisions of N_2 with thermal electrons, CO_2 , O_2^+ and other gases. (Walker, 1968.)

Since the problem with the observed ion densities is that O^+ densities are high and O_2^+ densities are low it is interesting to investigate the possibility that most of the directly ionized O_2^+ finds itself in an excited state such as ($a^4\Pi_u$). The charge exchange reaction between O_2^+ ($^4\Pi$) and $O(^3P)$ is exothermic. There is the possibility that this provides an effective channel for O_2^+ loss and O^+ production. However, this scheme will be nullified if the O^+ formed can charge exchange effectively again with $O_2(X^1\Sigma_g^+)$. In order to inhibit this process it is necessary to assume very high ion temperatures and extreme vibrational excitation of N_2 so that virtually all of the O^+ ions are converted to NO^+ . Furthermore, at high altitude dissociative recombination of O_2^+ provides an adequate source of loss and no special mechanism is required for O_2^+ disappearance. To cope with this fact it would be necessary to assume that ionization in the $^4\Pi$ state is inhibited at high altitudes or require that α_3 be unbelievably small there.

The density of the ion species detected at m/e equal to 4 is extraordinarily large if it is to be atmospheric He^+ (Fig. 2). Even if the He density at 116 km were 10^9 cm^{-3} the ionization rate would be only $10 \text{ cm}^{-3} \text{ sec}^{-1}$. Hence the lifetime of a He^+ ion would be 5 seconds which would imply a reaction rate between He^+ and N_2 of only $4 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$, more than 3 orders of magnitude slower than the laboratory value. Of course there has always been a problem in reconciling the apparently slow loss rate

for atmospheric helium ions in the upper ionosphere with these laboratory measurements. The problem has not been quite so severe as the present measurements would indicate. In view of this we would be reluctant to regard our observations as giving the atmospheric He^+ densities unless the data were unambiguous. This they are surely not. The altitude profiles are strange;—more signal was observed on the downleg, a large maximum occurring at 135 km; the scatter was large and a curious tendency noted for high and low values to alternate on successive sweeps. Since the Aerobee tanks are pressurized with He it is not inconceivable that our mass 4 species originated in our own vehicle. Therefore, until further evidence has been accumulated, we prefer not to place much credence in these data regarding He^+ .

Nevertheless, it is necessary to investigate the possibility that some of the other ions we observed were created by reactions involving He^+ . The following reactions can occur and all are fast:



If a steady state had been established at 116 km the He^+ loss rate would have been $3.5 \times 10^4 \text{ cm}^{-3} \text{ sec}^{-1}$. This is a rate overwhelmingly greater than the other ionization rates we have considered. The He^+ lifetime would be only about 10^{-3} sec if the rate constants listed above were valid in the upper atmosphere. The densities of other ionic species created by He^+ along would have been as follows

$$n_5^+ = 2.2 \times 10^2 \text{ cm}^{-3}$$

$$n_2^+ = 2.9 \times 10^2 \text{ cm}^{-3}$$

$$n_1^+ \geq 2.5 \times 10^3 \text{ cm}^{-3}$$

At 150 km we would have needed a production rate of $10^3 \text{ He}^+ \text{ ions cm}^{-3} \text{ sec}^{-1}$ and the ion densities traceable to He^+ would have been

$$n_5^+ = 3.7 \times 10^2 \text{ cm}^{-3}$$

$$n_2^+ = 1.5 \times 10^2 \text{ cm}^{-3}$$

$$n_1^+ = 2 \times 10^3 \text{ cm}^{-3}$$

Since N^+ would have been detectable if it were present in quantities as large as 10^2 cm^{-3} and did not appear even during the twofold enhancement in ionization which occurred near 130 km it is reasonable to assume that in fact the N^+ density was less than 50 cm^{-3} at most altitudes. Therefore it seems necessary to conclude that He^+ production of secondary ions was proceeding at a rate even lower than indicated above.

Even an N^+ density as small as 50 cm^{-3} would have serious potential consequences. At 116 km the production of O_2^+ from N^+ would have been at a rate of $2.5 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ and the production of NO^+ would have occurred at a rate of $1.8 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$. These are comparable to all other sources of O_2^+ and NO^+ . The enhanced production of O_2^+ would aggravate the already difficult problem of finding a sink for this ion.

The time constant for N^+ conversion to O_2^+ is about $2 \times 10^{-2} \text{ sec}$ and the decay time for O_2^+ is about 50 sec. If we imagine that the He^+ was being produced in a helium cloud diffusing from the rocket the very short time for conversion of He^+ to N^+ , N_2^+ and O^+ would provide insurance that

the He^+ density close to the mass spectrometer is the appropriate one for computing the production rates of those species. However, the rocket moved a significant distance during the time required for these ions in their turn to react. Thus most of the O_2^+ ions sampled at 116 km would have owed their existence to He^+ ions which had been formed at 116 km while the rocket was still relatively far away. If the N^+ density close to the rocket was 50 cm^{-3} it would have been considerably smaller than that at a distance of some 10 to 100 meters in front of the rocket. Thus if we assume that when the rocket arrived at the 116 km level outgassing had been proceeding for about 10 seconds in a medium where the average He diffusion coefficient was $10^7 \text{ cm}^2 \text{ sec}^{-1}$ the scale height of the helium cloud would have been 10^4 cm . Only during the time required for the rocket to travel the last 10^4 cm to the 116 km level would the O_2^+ production from N^+ have been of the order of $2 \times 10^3 \text{ sec}^{-1}$. This time was only about 0.1 seconds. Thus of all the O_2^+ ions sampled at 116 km only 200 would have been produced by N^+ ions created in the atmosphere by He^+ ions associated with the rocket. We conclude that if the helium originates from the rocket it only produces a minor perturbation in the ambient density of O_2^+ and NO^+ . Nevertheless, the problem presented by these He^+ observations is disturbing.

Extended discussion of optical excitation in this and other auroras will be reserved to other papers. The problem of green line excitation in particular will be treated in the paper following this one. (Donahue et al., 1969.) In anticipation of those discussions we shall briefly mention here an effect which we have observed several times. In some auroras we have found that the region of high efficiency for excitation of the (0 - 0) first negative band of N_2^+ and the $\text{OI } 5577\text{\AA}$ line extends considerably beyond that

for excitation of a variety of other emissions of N_2 and OI. An example is shown in Figs. 1 and 4 published by Donahue et al. (1968) where the maximum efficiency for the N_2 IPG and the OI 7774⁶Å line actually coincided with a minimum between two sizeable maxima in the efficiency for the 3914 band and 5577. We have examined several possible explanations for this effect. One of these is that the lower maximum in N_2^+ and $O(^1S)$ excitation is a result of acceleration of electrons deposited by the aurora near 120 km in a longitudinal electric field. This field is directed upward between 100 and 120 km and downward above 120 km. The source of this field we suggest is the excess negative charge density near 120 km created by deposition of the auroral primaries. During the aurora in question this deposition was at a rate of 5×10^3 electrons/cm⁻³ sec⁻¹ during a period lasting for at least 10^3 seconds. The field requirements can be deduced from the optical excitation conditions and the absence of electrons with energies greater than 100 eV according to the detector flow on the rocket. They are that the electric field component parallel to the magnetic field should be of the order of 50 mV m⁻¹. Such a value is needed to give the electrons drifting in the field an average energy of about 50 eV, too low to be detected by the electron analyzer (which in any event was insensitive to an electron beam collimated along the field lines) and too high to excite efficiently such states as the 3^5P term of O or the $B^3\Pi_g$ term of N_2 . The longitudinal component need not remain large over great distances.

We propose that even in the aurora discussed in this paper such a field was present and that the source of the field was at about 110 km. We suggest that ions created by electrons accelerated in the field below 110 km attained large velocities upward in the field and thus were not effectively

collected by the drawn-in field of the mass spectrometer. We also propose that the field at above 110 km was responsible for the large ion and electron "temperatures" (or high drift velocities) inferred in the region around 120 km. We recognize, however, that there will be a serious difficulty maintaining such large fields unless electron densities in the neighborhood are so low as to render the ordinary conductivity very low.

CONCLUSIONS

Conditions during a post break up auroral glow are such that O_2^+ ions are efficiently converted to NO^+ . Possible mechanisms for this conversion are charge exchange of O_2^+ with NO , an ion molecule reaction between O_2^+ and N or an accelerated four center reaction of O_2^+ and N_2 caused by vibrational excitation of N_2 . Very large NO and/or N densities would be required to effect the conversion at the rate required. O^+ and diatomic ion removal rates imply elevated ion and electron temperatures.

The low density of O_2^+ precludes its playing a major role in producing the auroral green line except at high altitude.

Some features of the ion distributions suggest that there may be large longitudinal electric fields in the aurora. There is optical evidence also for such high fields, despite the fact that it seems to be impossible to maintain them in the presence of the high ordinary conductivity of the auroral ionosphere.

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FIGURE CAPTIONS

- Fig. 1. Sample record of the mass spectrometer output during flight 4.217 UA, February, 1968.
- Fig. 2. Ion densities measured on ascent of flight 4.217 UA, February, 1968 Ft. Churchill. The volume emission rate for the (0 - 0) first negative band of N_2^+ is also plotted.
- Fig. 3. Rate constants required to account for O^+ removal as a function of altitude, k_b is the rate constant for O^+ , O_2 charge exchange, k_c for O^+ reaction with N_2 . Curves drawn through the bases of the arrows represent self consistent values at the same T_1 and no N_2 vibrational excitation. Values at tips of arrows presume an enhancement of k_c because of vibrational excitation. Corresponding O^+ temperatures are shown as well as the electron temperature implied by the dissociative recombination coefficients needed.
- Fig. 4. Density of NO (n_4), of N (n_5) or rate constant for O_2^+ , N_2 reaction (k_g) needed to account for the O_2^+ and NO^+ densities observed. The horizontal bars on the left represent lower limits.
- Fig. 5. He^+ densities measured during flight 4.217 UA.

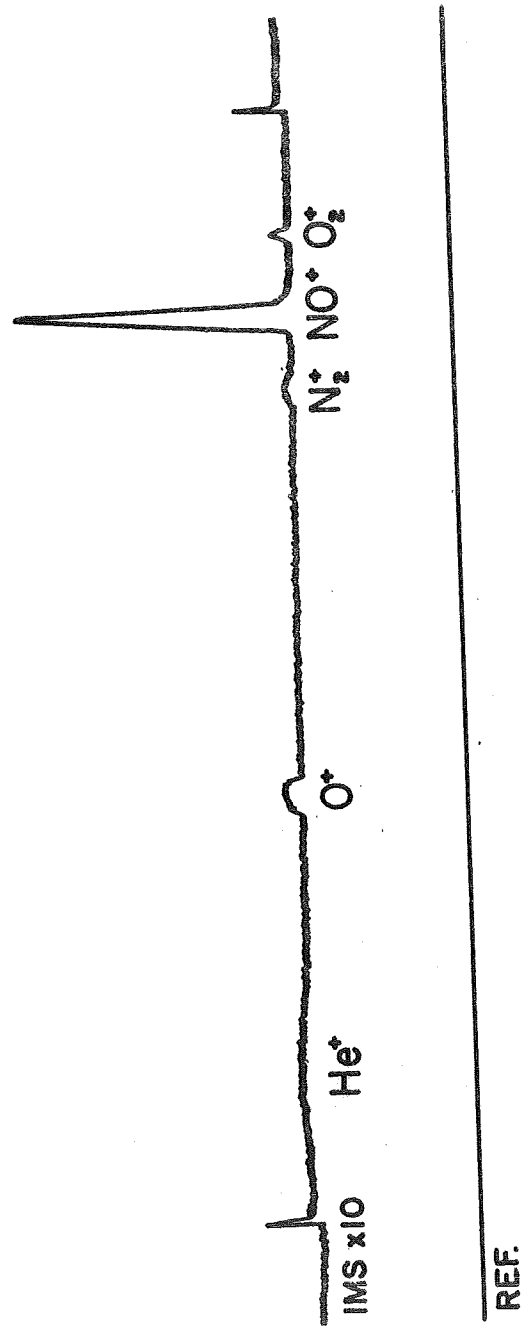


Figure 1

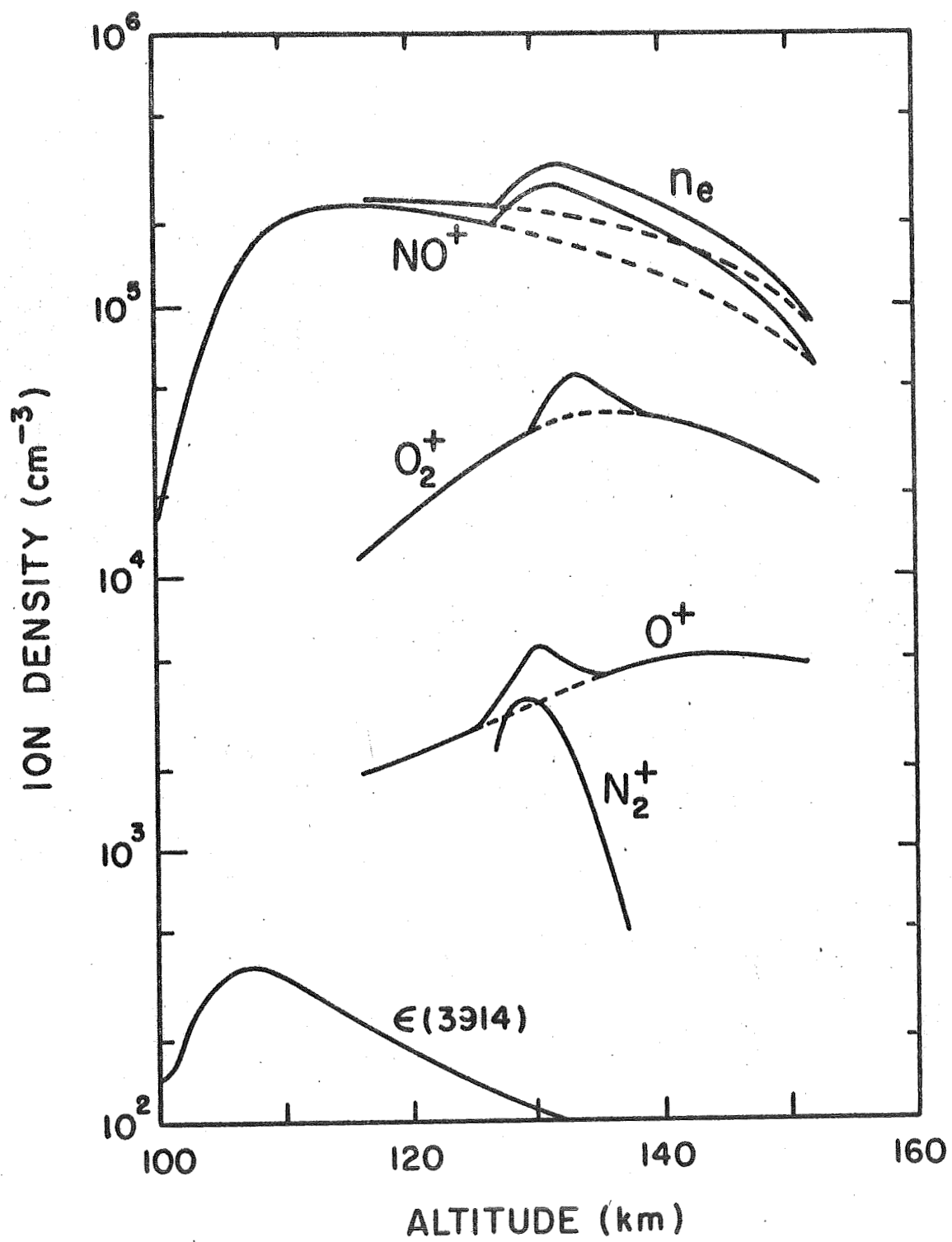


Figure 2

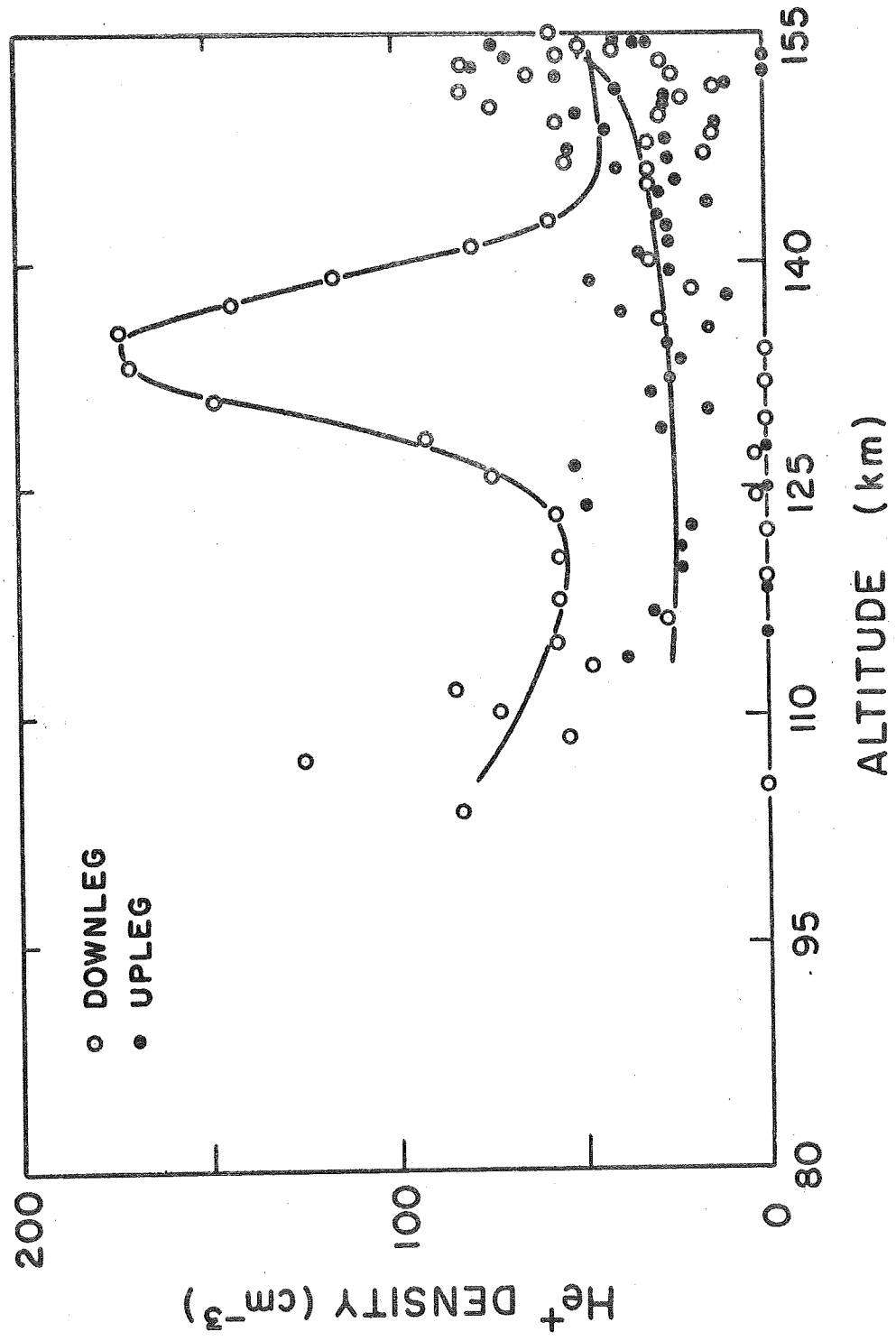


Figure 3

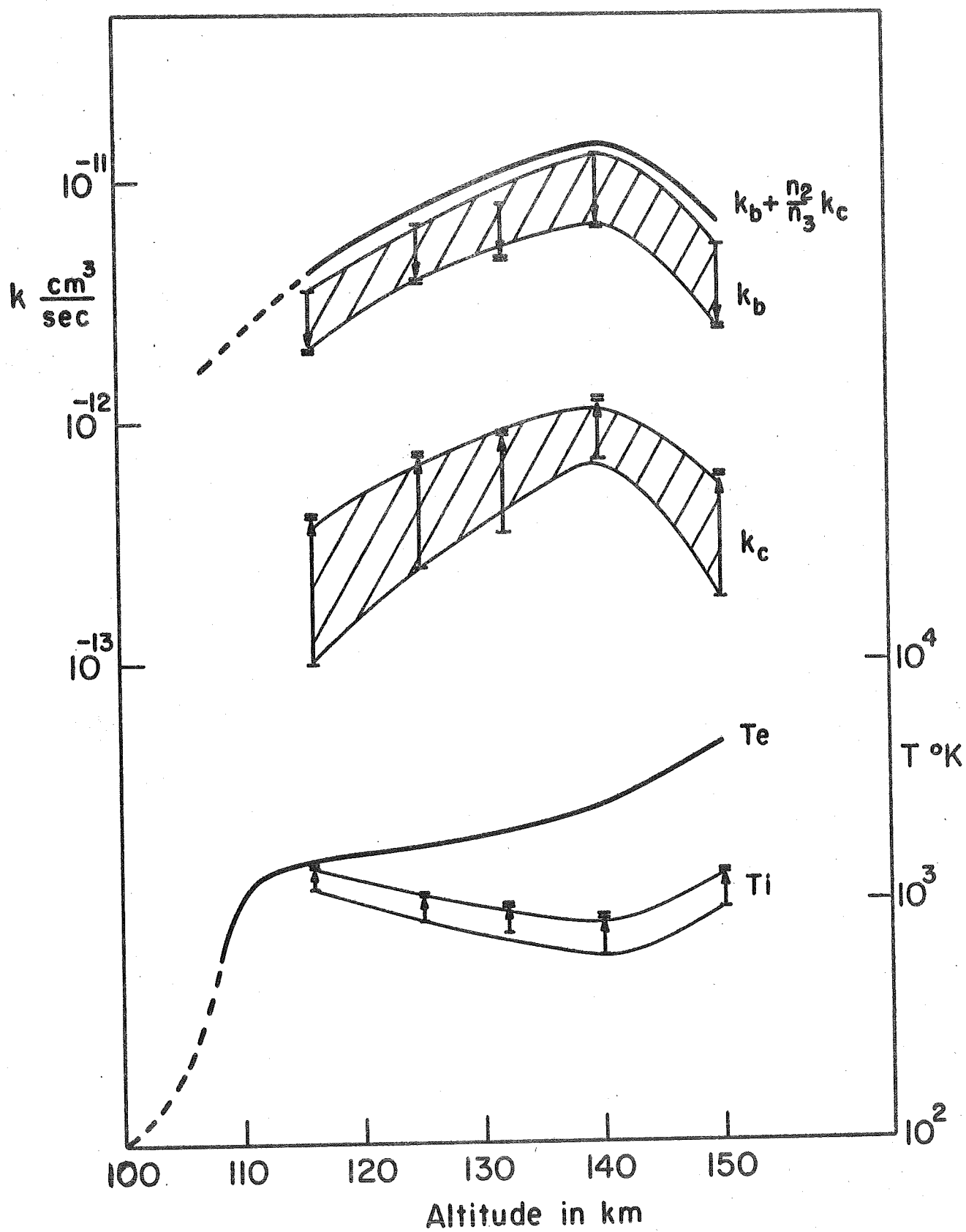


Figure 4

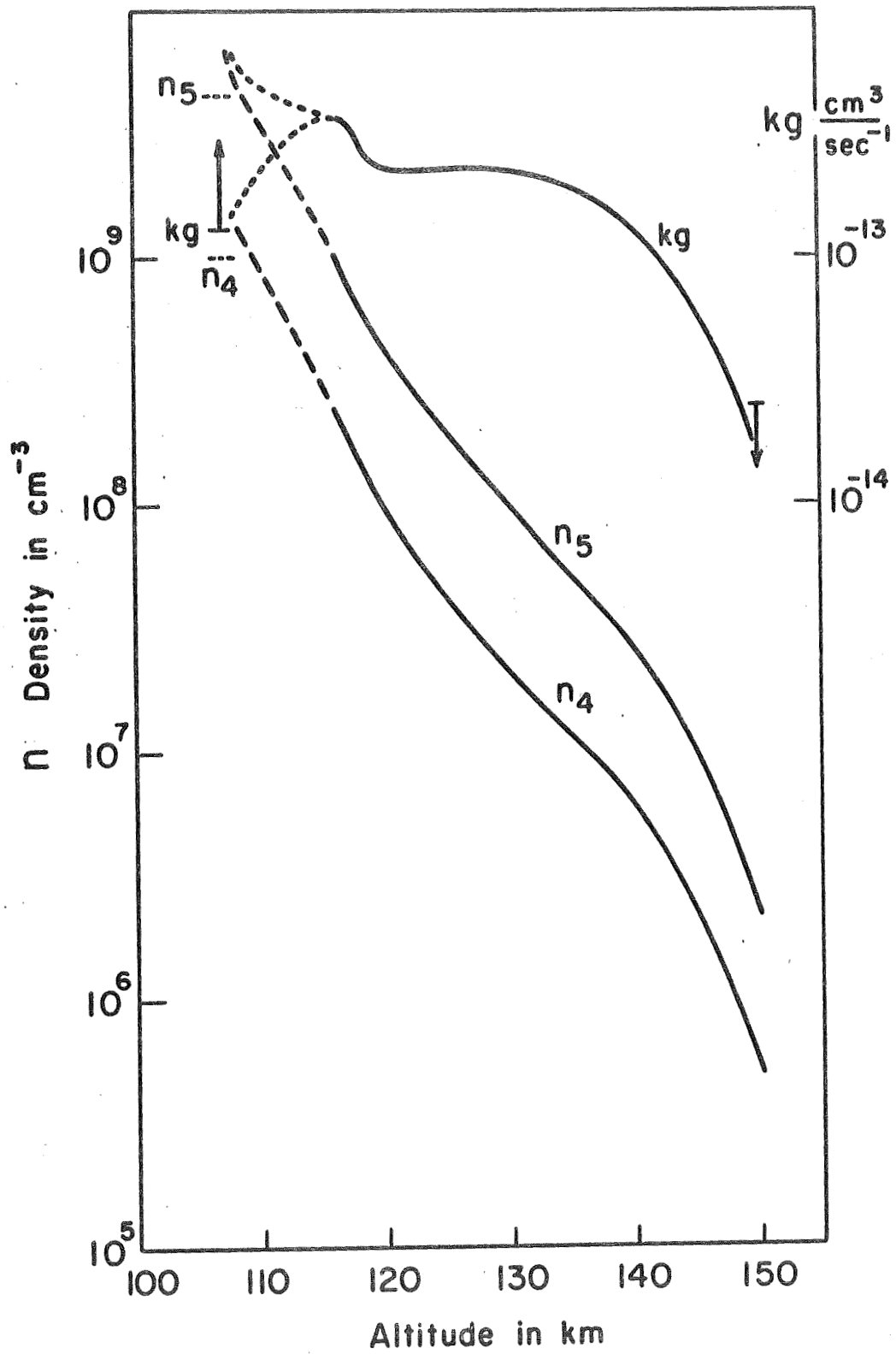


Figure 5

